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Laboratory and Field Evaluation of NS-100 Reverse Osmosis Membrane

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16. ABSTRACT

Laboratory life tests were conducted with B-9 and NS-100 reverse osmosis (RO) membranes treating zinc cyanide plating solution at 10% of bath strength. The B-9 membrane was degraded by the high pH of the solution which was beyond the upper pH limit (pH 11) recommended for this membrane. The NS-100 membrane showed little deterioration in performance over the first 500 hours of operation. A reduction in permeate flux and rejection after 500 hours appeared to be due to precipitation of salts which resulted from operation in the closed loop test system and would not be expected in actual field operation.

Field tests were conducted at New England Plating Company treating rinsewater from the zinc cyanide plating operation with a module of seven tubular NS-100 reverse osmosis membranes. Conductivity rejections of 80-96% and zinc rejections of 96-99.7% were measured at flux levels of 0.20-0.37$m^3/m^2/day$ (5-9 $gal/ft^2/day$). During 2300 hours of exposure to the rinsewater, the membrane showed no degradation in performance as determined by NaCl performance tests and standard tests with a solution of zinc cyanide plating bath diluted to 5% of bath strength.

A number of attempts were made to fabricate an NS-100 spiral-wound module, but all were unsuccessful. Further development will be required before the NS-100 can be commercially offered in an economically attractive configuration.

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LABORATORY AND FIELD EVALUATION OF NS-100 REVERSE OSMOSIS MEMBRANE

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is a product of the above efforts. It was undertaken to demonstrate the effectiveness and economic feasibility of using reverse osmosis for closed-loop control of metal finishing rinse wastes uder actual plant conditions. The reverse osmosis system concentrates the chemicals for return to the processing bath while purifying the wastewater for reuse in the rinising operation. The results of the report are of value to R & D programs concerned with the treatment of wastewaters from various metal finishing, non-ferrous metal, steel, inorganic, and other industries. Further information concerning the subject can be obtained by contacting the Metals and Inorganic Chemicals Branch of the Industrial Pollution Control Division.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

Laboratory life tests were conducted with B-9 and NS-100 reverse osmosis (RO) membranes treating zinc cyanide plating solution at ten percent of bath strength. The B-9 membrane was degraded by the high pH of the solution, which was beyond the upper pH limit (pH 11) recommended for this membrane. The NS-100 membrane showed little deterioration in performance over the first 500 hours of operation. A reduction in permeate flux and rejection after 500 hours appeared to be caused by the precipitation of salts that resulted from operation in the closed loop test system and would not be expected in actual field operation.

At the New England Plating Company, field tests were conducted treating rinsewater from the zinc cyanide plating operation with a module of seven tubular NS-100 reverse osmosis membranes. Conductivity rejections of 80-96 percent and zinc rejections of 96-99 percent were measured at flux levels of 0.20-0.37 m^3/m^2/day (5-9 gal/ft^2/day). During 2,300 hours of exposure to the rinsewater, the membrane showed no degradation in performance as determined by NaCl performance tests and standard tests with a solution of zinc cyanide plating bath diluted to five percent of bath strength.

Because of the high cost per unit membrane area of tubular RO modules, a number of attempts were made to fabricate a NS-100 spiral-wound module. These attempts were all unsuccessful, and it is concluded that a more extensive development program will be required before the NS-100 membrane can be offered commercially in an economically attractive configuration. Recently, a new membrane similar to the NS-100 has been developed in a spiral-wound configuration. This membrane, designated PA-300, shows promise of superceding the NS-100 membrane for plating waste applications.

This report was submitted in fulfillment of Grant No. R803753 by the American Electroplaters' Society, Inc. under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period June 1, 1975 to April 15, 1976 and work was completed as of June 1, 1978.

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SECTION 1

INTRODUCTION

The discharge of used rinsewaters from metal finishing operations is a major source of water pollution in the electroplting industry. Various techniques are available for treating the rinsewater generated in the electroplating process. During recent years, increased attention has been focused on closed-loop systems used to reclaim rinsewater from individual plating baths. In these systems, the chemicals dissolved in the rinsewater discharge are concentrated for return to the plating bath. The purified water produced in the process can be reused for rinsing.

Reverse osmosis (RO) is one of several concentration techniques that can be used for closed-loop treatment of electroplating rinsewaters. When pressurized rinsewater (feed) is brought in contact with a semi-permeable membrane, water passes through the membrane at a much higher rate than the dissolved salts. The process produces a low concentration/high volume "permeate" stream, which is recycled to the rinsing operation, and a high concentration/low volume "concentrate" stream, which is returned to the plating bath. Membrane performance is generally characterized in terms of flux (the flow rate of permeate produced per unit membrane area) and rejection (the percent concentration differecne between the feed and permeate streams), both measured at specified conditions. Advantages and limitations of RO for closed-loop treatment of electroplating rinsewaters have been discussed previously (1).

Preliminary tests have been conducted (1) to assess the applicability of the commercially available membranes (cellulose acetate and polyamide) to a variety of different electroplating rinsewaters. While the membranes were effective in concentrating dissolved species for all the plating baths, membrane life was judged to be insufficient for use in certain rinsewaters with extremes of pH or high oxidant (chromic acid) levels.

Several RO field tests have been conducted to determine the applicability of RO under practical conditions. These have included:

-- spiral-wound cellulose acetate for treatment of Watts-nickel rinsewater (2).

-- hollow fiber polyamide for treatment of Watts-nickel rinsewater (3).

-- hollow fiber polyamide for treatment of copper cyanide rinsewater (4).

These field tests indicate that either the cellulose acetate or polyamide membrane can be used to treat Watts-nickel rinsewaters, and the economics of this application can be quite attractive. On the other hand, treatment of copper cyanide rinsewaters cannot be considered a proven application since, during one of two field tests, the rate of membrane deterioration would result in excessive costs for membrane replacement.

In general, previous work has indicated that membrane life is critical in determining the applicability of RO to rinsewater recovery, and that pH is an important parameter in membrane life. For the cellulose acetate membrane, life is generally adequate over a pH range of 2.5-7; for the polyamide membrane, life is generally adequate over a pH range of 4-11.

The objective of the work covered by this report was to extend the applicability of RO to the high-pH cyanide rinsewaters. In particular, zinc cyanide was selected because of its high pH and its high volume usage in the plating industry. Because of the pH limitations of the commercially available membranes, a non-commercial membrane, NS-100, was to be tested and developed in a spiral-wound configuration for electroplating applications. Previous tests with this membrane have indicated good stability over a pH range of 1-13 (5).

SECTION 2

CONCLUSIONS

Laboratory life tests indicated that the NS-100 membrane is chemically resistant to zinc cyanide rinsewater at ten percent bath strength (rinsewater pH = 12.0-12.5). On the other hand, the performance of the commercially available B-9 membrane deteriorated with time, probably as a result of chemical degradation, since the pH of the test solution was beyond the recommended range (4-11) for this membrane.

Membrane fouling, which was observed in the laboratory life tests after 500 hours of operation, was probably the result of the buildup and precipitation of a sparingly soluble salt within the closed-loop test system. This type of fouling would not be anticipated in a practical system.

During a 2300-hour field test with a tubular NS-100 module, flux levels of 0.20-0.37 $m^3/m^2/day$, conductivity rejections of 80-96 percent, and zinc rejections of 96-99.7 percent, were obtained and remained stable throughout the test. There was no degradation of the membrane as determined by a standard NaCl solution test and a standard test with zinc cyanide solution diluted to 5 percent of bath strength.

Attempts to fabricate the NS-100 membrane in a spiral-wound configuration were unsuccessful. A more extensive development effort will be required before the NS-100 membrane can be offered in an economically attractive configuration for electroplating applications.

SECTION 3

RECOMMENDATIONS

Considering both the imminent commercialization of the PA-300 membrane in a spiral-wound configuration and the similarity of the PA-300 to the NS-100 in type and chemistry, tests should be conducted with the PA-300 membrane to evaluate its performance and stability for treatment of zinc cyanide rinsewaters. If the results look promising, field tests should be conducted to evaluate the performance of spiral-wound PA-300 modules for treatment of actual zinc cyanide rinsewaters. (These recommendations are implemented under EPA Grant Nos. R8043311 and R805300. Full results will be included in the final reports for these grants).

Further development of the NS-100 membrane should be suspended until the PA-300 and other membrane materials have been evaluated for the treatment of various electroplating rinsewaters.

SECTION 4

LABORATORY LIFE TESTS WITH NS-100 AND B-9 MEMBRANES

The objective of this program was to demonstrate the feasibility of using RO for closed-loop treatment of the rinsewaters resulting from zinc cyanide plating operations. Because of the high pH of zinc cyanide rinsewater, a laboratory life test was conducted to determine whether the du Pont B-9 polyamide membrane could be used in the field tests. When this program was initiated, the polyamide membrane was the only commercially available membrane that could withstand alkaline conditions (pH 4-11). The other commercially available membranes, namely cellulose acetate and cellulose triacetate, are limited to pH values below about 8.0.

In parallel with these tests, a laboratory life test was conducted with the NS-100 developmental membrane to determine if this membrane could be used for the field test in the event that the B-9 membrane was degraded by the zinc cyanide rinsewater. The NS-100 membrane has exhibited good stability over a pH range of 1-13 (5).

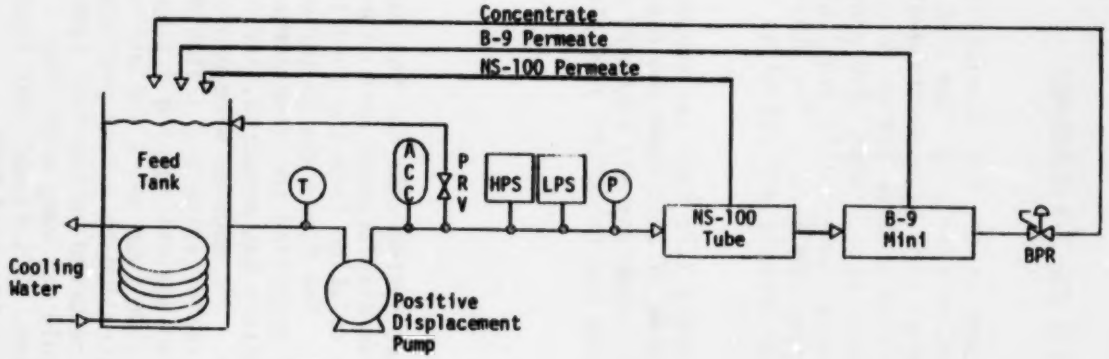
EXPERIMENTAL PROCEDURE

Laboratory Life Test System

A simplified flow schematic of the test system used for the laboratory life tests is shown in Figure 1. A positive displacement pump (Yarway Cyclophram Model 072) was used to withdraw solution from the feed tank and pressurize it to 2.8×10^6 N/m^2 (400 psig). The flow rate to the modules was controlled at 0.12 m^3/hr (0.53 gpm) by adjusting the displacement volume of the pump. The pump discharge pressure was measured, and pressure pulsations were dampened by an accumulator. The modules were protected against over-pressurization by a pressure relief valve and a high pressure switch. In addition, the pump was protected against running dry by a low pressure switch. Feed passed through a NS-100 tube and a B-9 mini-permeator in series, with the operating pressure controlled by a back pressure regulator. Concentrate and both permeates were returned to the feed tank (total recycle) so that the feed concentration would not vary with time. The feed temperature was measured at the pump suction. Frictional heat input from the pump was removed by a cooling coil placed in the feed tank.

Membrane Modules

The B-9 polyamide membrane was in the form of a mini-permeator. The design of a mini-permeator is shown in Figure 2. The active portion of the permeator consists of one strand (150 filaments) of polyamide hollow fibers.



Key:

T	Temperature Gauge
ACC	Accumulator
PRV	Pressure Relief Valve
HPS	High Pressure Switch
LPS	Low Pressure Switch
P	Pressure Gauge
BPR	Back Pressure Regulator

Figure 1. Flow schematic for laboratory life test system.

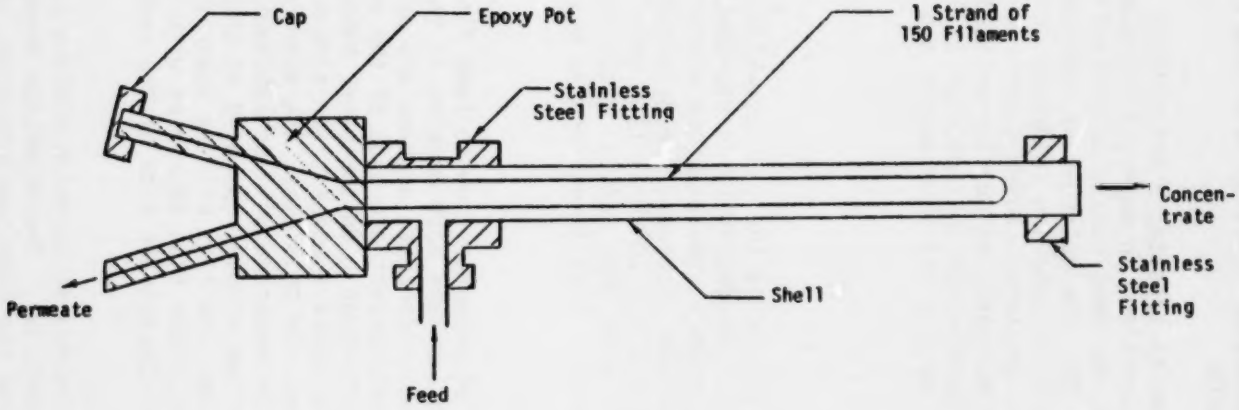


Figure 2. Schematic drawing of a B-9 mini-permeator.

The strand is looped as shown, and both ends are sealed in an epoxy pot. Permeate is withdrawn from one end of the fiber strand after slicing exposes the open fiber ends. A normal four-inch diameter permeator contains about 900,000 filaments; so the mini-permeator contains less than 2×10^{-4} of the surface area of a full-scale module.

The NS-100 membrane is formed by treating a polysulfone membrane support with a solution of PEI (polyethylenimine) in water, a solution of TDI (2,4-tolylene diisocyanate) in hexane, and heat curing to cross-link the PEI. Before reaction with the PEI and TDI, the polysulfone membrane is essentially an ultrafiltration membrane capable of removing suspended solids and macromolecules. The PEI/TDI/heat-cure treatment causes a skin to form at the membrane surface that is capable of rejecting smaller molecules and dissolved salts. The NS-100 membrane is supported on the interior wall of an epoxy-impregnated fiberglass tube 12.7 mm (0.5 in) in diameter and 0.61 mm (2.0 ft) long.

Performance Parameters

Productivity--

The productivity of a given module is the rate at which permeate is produced under specific conditions. Productivity is dependent on temperature, pressure, and feed concentration at the membrane surface. Where slight variations in the operating conditions occurred, the measured productivity of the mini-permeator was corrected to 2.8×10^6 N/m^2 (400 psig) and 25°C (normal operating conditions for the du Pont module) using data from the du Pont Technical Information Manual. Flux is defined as productivity per unit membrane area.

Conversion--

The conversion is the ratio of permeate flow to feed flow. For a module operating at near-zero conversion (as were both modules in the life test), the concentrations of the feed and concentrate streams are nearly the same. Thus, the concentration on the feed/concentrate side of the membrane is very nearly the same as the feed concentration. On the other hand, a module operated at high conversion will produce a concentrate stream having a higher concentration than the feed stream. In this case, the average concentration on the feed/concentrate side of the membrane will be substantially higher than the feed concentration. For two modules operated at the same pressure, temperature, and feed concentration, the flux will be lower for the module operated at the higher conversion, since flux decreases with increasing average concentration on the feed/concentrate side of the membrane.

Rejection--

The rejection (r) measures the degree to which plating salts are prevented from passing through the membrane. The rejection depends on the operating pressure, the conversion, and the feed concentration, and is defined by:

$$r = \frac{100\,[C_f - C_p]}{C_f}$$

where C_f = feed concentration (conductivity)
C_p = permeate concentration (conductivity).

Operating Conditions

The feed solution used in the life tests was prepared by diluting a sample of zinc cyanide plating bath from New England Plating Company to ten percent of bath strength (volumetric basis). The nominal bath composition is given below:

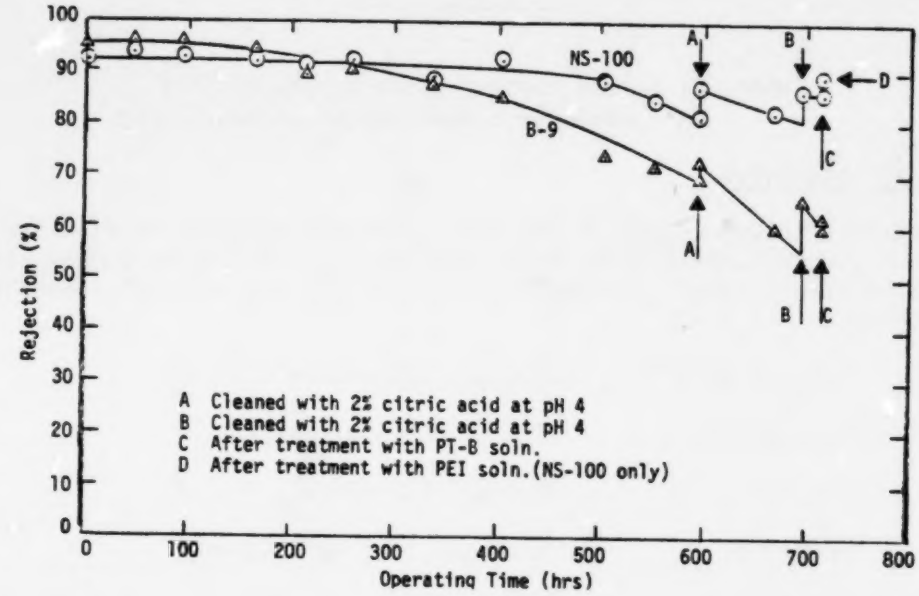
zinc (as metal)	15.0 g/l (2.0 oz/gal)
free cyanide	19.5 g/l (1.6 oz/gal)
caustic	75.0 g/l (10 oz/gal)
carbonate	50-60 g/l (7-8 oz/gal) avg
brightener	0.5% (vol)

The test system was operated continuously on the zinc cyanide feed solution, except during interruptions for maintenance and NaCl performance tests.

The decline in rejection performance is readily indicated by the NaCl tests, since rejection is most sensitivve for small univalent ions. The NaCl performance tests were conducted every two days to obtain control data on the membrane flux and rejection. After disconnecting the zinc cyanide feed tank and draining the remainder of the system, a feed tank containing a 1,500 mg/l solution of NaCl was connected, and the system was operated at 1.8×10^6 N/m^2 (400 psig), 2.0 l/min flow rate, and 25°C until steady state was reached. At this time the NaCl productivity and NaCl rejection were measured for each module. The system was drained and returned to closed-loop operation on the zinc cyanide solution.

RESULTS AND DISCUSSION

NaCl rejections and productivities for the two membranes, measured approximately every 48 hours, are shown in Figure 3 as a function of operating time. The productivity for the NS-100 increased over the first 500 hours from 7 to 8.5 cm^3/min. However, between 500 and 600 hours, the productivity decreased substantially to only 3.6 cm^3/min. This decrease is largely the result of membrane fouling. When the membrane was cleaned with a two percent citric acid solution (A), the productivity was restored to its initial value. However, when the productivity again declined rapidly, a second cleaning with citric acid (B) increased the productivity but did not restore it to its initial value. After treatment with PT-B, a du Pont proprietary membrane


Rejection (%)
Operating Time (hrs)
NS-100
B-9
A Cleaned with 2% citric acid at pH 4
B Cleaned with 2% citric acid at pH 4
C After treatment with PT-B soln.
D After treatment with PEI soln.(NS-100 only)

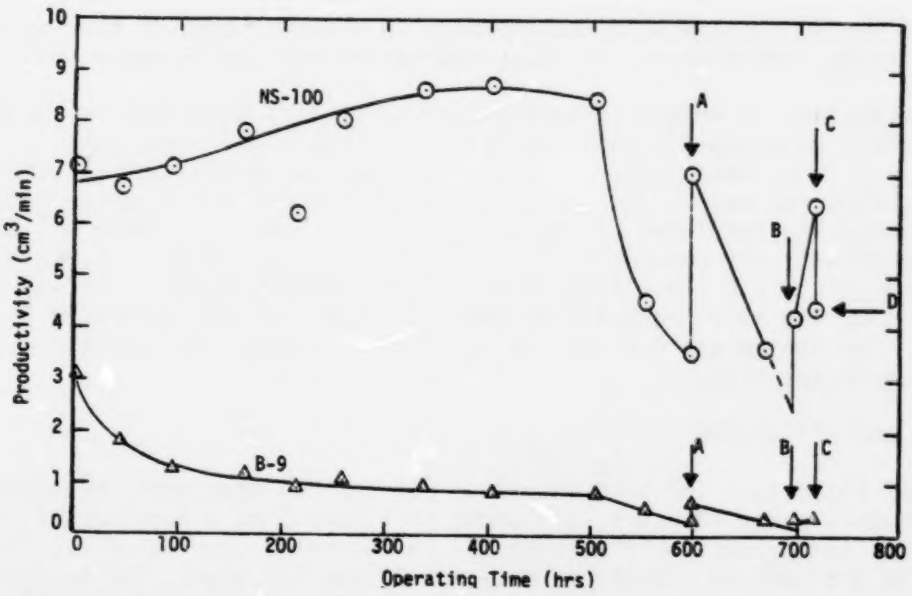


Figure 3. Rejections and productivities vs. operating time for the NS-100 and B-9 membranes.

"tightening agent," the productivity increased almost to its initial value (C), but dropped after treatment with a PEI solution (D).

The productivity for the B-9 membrane decreased rapidly to about one-third of its initial value and appeared to be leveling off until about 500 hours. A rapid decline in productivity was again observed between 500 and 600 hours and between 600 and 700 hours. Only modest improvements in productivity were obtained after cleaning and PT-B treatment.

The rejection for the NS-100 was very stable over the first 500 hours, but there was a substantial decline in rejection between 500 and 600 hours and between 600 and 700 hours. This decline corresponds exactly with the productivity decline discussed above. Citric acid cleaning and PEI treatment restored the rejection of the NS-100 to its initial value.

The rejection for the B-9 decreased substantially over the life test and could not be restored by citric acid cleaning or PT-B treatment. Even over the first 500 hours, where the rejection for the NS-100 remained constant, the rejection for the B-9 declined substantially.

One of the most striking features of these data is the difference in membrane performance before and after 500 hours of operating time. Apparently, some type of membrane fouling occurred after 500 hours. The cleaning solution (two percent citric acid at pH 4) was selected to remove iron hydroxide precipitate, which could have resulted from corrosion of stainless steel components in the test system. However, if this were the foulant, performance should have declined gradually from the beginning of the life test. A more satisfactory explanation is that some constituent in the feed builds up to its solubility limit over the first 500 hours of operation and, thereafter, continues to foul the membrane by precipitation. This hypothesis is supported by the presence of a precipitate in the feed tank that was quite evident after 720 hours and may have started to accumulate at about 500 hours. The feed solution was analyzed for carbonates, with the thought that the dissolution of CO_2 could increase the carbonate level and cause precipitation of Na_2CO_3. The analysis showed that Na_2CO_3 was considerably below its solubility limit; however, precipitation of some less soluble carbonate species cannot be ruled out.

If the hypothesis is correct that the total-recycle mode of operation resulted in an accumulation of sparingly soluble salt, the data beyond 500 hours operating time would not be characteristic of membrane performance under actual operating conditions. Even if the bath were saturated with this salt, the drag-out would be diluted in the rinse and concentrated in the RO system to only about ten percent of bath strength, that is, ten percent of saturation. Hence, the sparingly soluble salt would not accumulate in the reverse osmosis system as it does during total recycle.

Based on the first 500 hours of operation, the decline in both flux and rejection for the B-9 is too rapid to make this membrane economically attractive for zinc cyanide recovery. This conclusion is supported by the results of static tests conducted by du Pont. In these tests the polyamide hollow fiber was soaked in a zinc cyanide solution at ten percent of bath strength.

Significant deterioration of the physical strength of the fibers was observed during several weeks of testing.

Over the first 500 hours of operation, the flux and rejection for the NS-100 were good. It was concluded that the NS-100 membrane has potential for the treatment of zinc cyanide rinsewaters and should be field tested on actual rinsewaters from a zinc cyanide plating operation.

SECTION V

FIELD TEST OF THE NS-100 MEMBRANE

ATTEMPTS TO FABRICATE AN NS-100 SPIRAL-WOUOND MODULE

Following the laboratory life tests with the B-9 mini-permeator and the NS-100 tubular membrane it was decided that the most meaningful field test would be one conducted with the NS-100 membrane in the spiral-wound configuration. The spiral-wound configuration is preferred for treating plating rinsewaters since the capital and operating costs are lower, and the advantages of the tubular configurations (namely, resistance to fouling by suspended solids and operation at higher pressures) are not required in this application. The construction details of a spiral-wound module are shown in Figure 4.

The conditions and procedures used for formation of the NS-100 were similar to those used for preparation of NS-100 tubular membranes (6). Following the laboratory life test, four attempts were made to fabricate a workable NS-100 spiral-wound module. The first three attempts failed because of leaks in the module glue seams. Better results were obtained with the fourth module. This module, which contained a membrane surface area of about 2.3 m^2, was tested on a total-recycle system similar to that shown in Figure 1. The module was operated on a 1,500 ppm NaCl feed solution at 2.8 x 10^6 N/m^2, 25°C, and approximately zero percent conversion. No gross leaks were observed, but a considerable break-in period was required in order to achieve the final steady state flux and rejection. After 24 hours of operation, the flux was approximately 0.53 $m^3/m^2/day$ (13 gfd) and the rejection was 75 percent. While these results are encouraging, the performance of this module is inadequate for a meaningful field test. The NS-100 membrane is capable of achieving rejections in excess of 98 percent under the conditions at which the module was tested.

Since attempts to fabricate a NS-100 spiral-wound module were unsuccessful, it was decided to proceed with field testing the NS-100 membrane in the tubular configuration. It was reasoned that these tests would illustrate the performance of the membrane over an extended period of exposure to rinsewater under actual field conditions. If these tests were successful, further development of a spiral-wound module would be warranted.

EXPERIMENTAL PROCEDURE

A flow schematic of the reverse osmosis system used to field test the tubular NS-100 membrane is shown in Figure 5. Feed was pumped from the rinse tank by a booster pump (Worthington Model D-520) and filtered through a 30-micron and a 1-micron cartridge filter arranged in series. The pressure

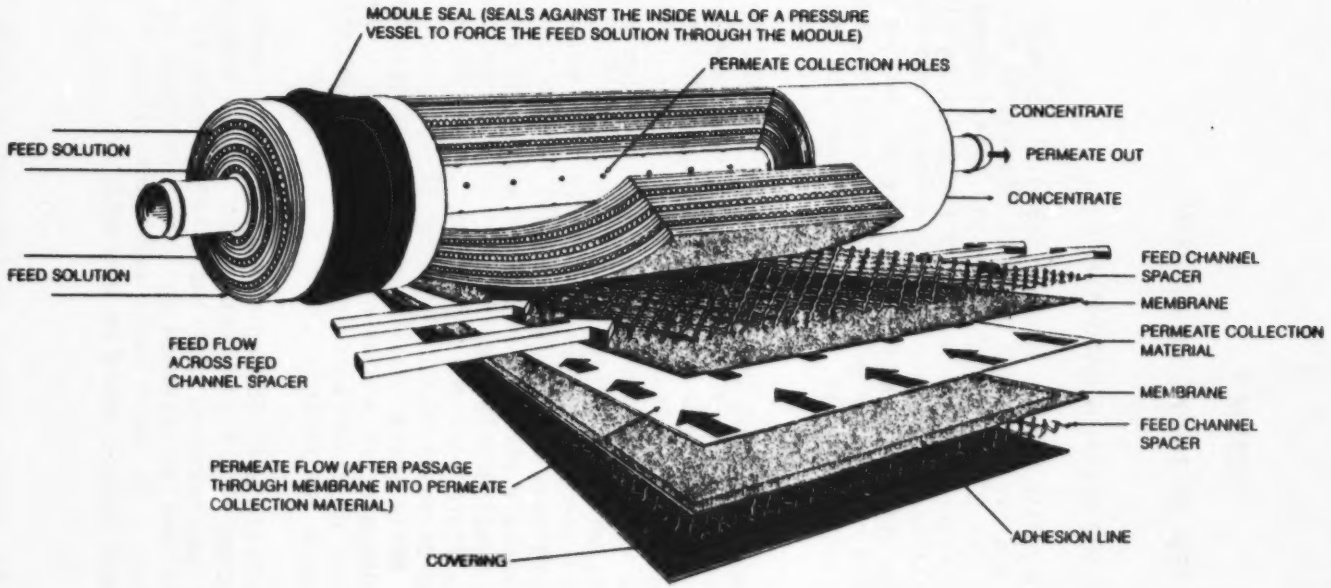
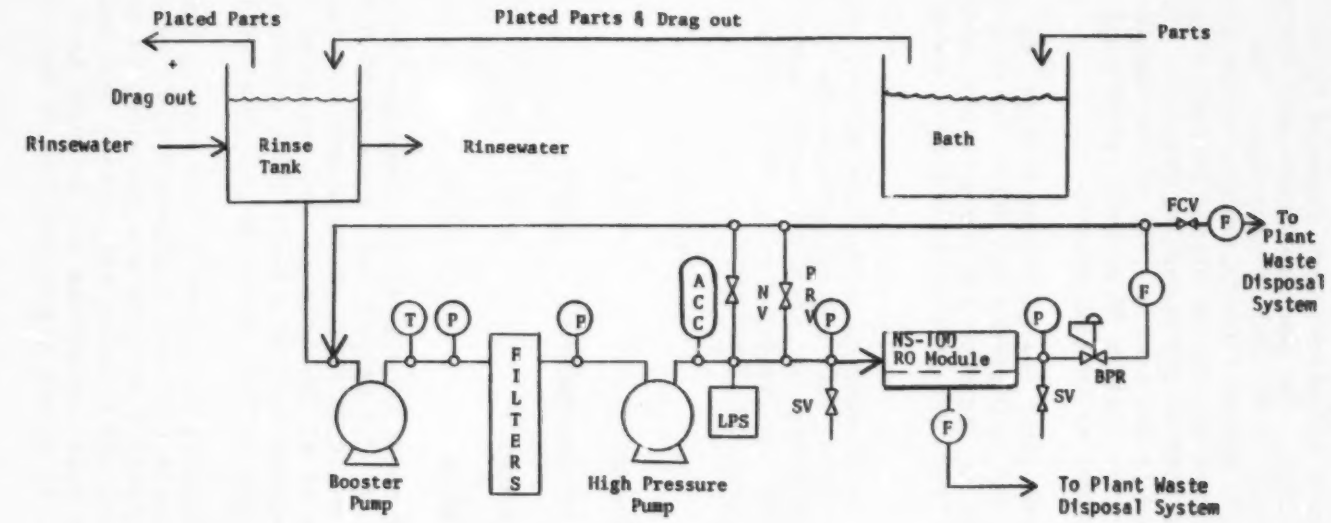


Figure 4. Abcor spiral-wound membrane module.



Key:

T	Temperature Gauge
P	Pressure Gauge
ACC	Accumulator
LPS	Low Pressure Switch
NV	Needle Valve
PRV	Pressure Relief Valve
SV	Sample Valve
BPR	Back Pressure Regulator
F	Flow Meter
FCV	Flow Control Valve

Figure 5. Flow schematic for field test system.

of the filtered feed was then increased to the desired operating pressure of 4.2×10^6 N/m^2, (600 psig) by a positive displacement diaphragm pump (Yarway Cyclophram Model 072). Pressure pulsations were dampened by an accumulator located on the pump discharge. The membrane tubes were connected in series with a flow rate of 2.5 m^3/day (0.45 gpm) in each tube. The permeate stream from the tubular NS-100 module flowed directly to the plant wastewater treatment system. The concentrate stream passed through a back pressure regulator, which was used to control the operating pressure. Most of the concentrate stream was returned to the suction side of the booster pump while a small portion (sufficient to yield a 90 percent conversion) was bled through a control valve to the plant wastewater system.

Pressures were measured before and after the cartridge filters, to determine when replacement was necessary, and before and after the reverse osmosis module to determine the operating pressure and pressure drop along the tubes. The system was protected from over-pressurization by a pressure relief valve.

Feed and concentrate flow rates were measured using flow meters, while the permeate flow rate from each individual tube was measured by the "bucket and stopwatch" technique. Feed, concentrate, and permeate samples were taken periodically for analysis. Samples were analyzed for zinc, total solids, pH, and conductivity using the following analytical methods:

Parameter	Method	Procedure
Zinc	Atomic absorption	301A*
Total solids	Evaporation-gravimetric	208A*
pH	Meter reading	424*
Conductivity	Meter reading	205*

The membrane module consisted of seven tubular NS-100 membranes arranged in series. Each tube had a diameter of 12.7 mm (0.5 in), a length of 0.61 mm (2 ft), and a surface area of 0.024 m^2 (0.26 ft^2), (tubular module total area = 0.17 m^2). Two different types of NS-100 membrane were installed in the module: four tubes of Type I membrane cast on a 4-mil-thick polysulfone backing, and three tubes of Type J, cast on 8-mil-thick polysulfone backing.

Membrane performance was determined by periodically interrupting the field test and conducting a total recycle test with a standard solution at standard operating conditions. The standard solution was contained in an auxiliary feed tank and, after draining and flushing the system, feed was withdrawn from the auxiliary tank and both concentrate and permeate were returned to the tank (see Figure 1). At steady state, the flux of each tube

*Standard Method for the Examination of Water and Wastewater, 14th ed., American Public Health Association, Washington D.C. 1976.

was measured and samples of feed and permeate were obtained to determine the rejection for each tube. Following the test, the system was drained and returned to operation on the actual zinc cyanide rinsewater.

Standard performance tests were conducted with two different solutions: a 1,500 ppm NaCl solution, and a solution of the actual zinc cyanide plating bath diluted to five percent of bath strength. During these tests the system was operated at 4.2×10^6 N/m^2 (600 psig), 25°C (77°F), and 2.5 m^3/day/tube (0.45 gpm/tube) feed rate.

Results of previous field tests have shown that performance data obtained during operation on the actual rinsewater are difficult to interpret since there is no way to control the concentration of the feed to the RO system. Since feed concentration affects both flux and rejection, data obtained at different feed concentrations cannot be directly compared to determine whether the flux and rejection remain stable with time. This problem, varying feed concentration, is obviated by using the standard zinc cyanide solution and total recycle operation.

RESULTS AND DISCUSSION

During the tests, the module with seven tubular membranes was exposed to zinc cyanide rinsewaters for 2,300 hours, with an actual operating time of 1,300 hours. The shorter operating time reflects uncontrollable system interruptions at the site, as well as minor mechanical problems that mainly occurred during the first 1,000 hours of membrane exposure. Permeate fluxes and solute rejections for both types of membrane showed little decline in performance throughout the test. The Type J membranes (8-mil backing) displayed higher rejections than the Type I membranes (4-mil backing), presumably because of the improved physical properties. Accordingly, only data for the Type J membranes are presented.

The rejections obtained during standard tests with zinc cyanide rinsewaters (plating bath diluted to five percent of bath strength) for the three Type J tubular membrane assemblies are presented in Figures 6 through 8. Each figure presents the rejection data obtained for one of the three Type J tubes tested. The rejections were excellent. They appeared to increase during the first 1,500 hours, then remained constant or decreased slightly during the remainder of the test. Conductivity rejections were 80-96 percent, total solids rejections 87-96 percent, and zinc rejections 96-99.7 percent.

Fluxes obtained during the tests at five percent of bath strength were also very stable. They are presented in Figure 9, which indicates flux levels of 0.20-0.37 m^3/m^2/day.

The conductivity rejections obtained with 1,500 ppm NaCl solutions are given in Figure 10. The rejection appeared to decrease with time, but this is believed to have resulted from an ion exchange or adsorption phenomenon occurring when the membranes were in contact with the highly alkaline zinc cyanide rinsewaters. This hypothesis was substantiated by operating the system on a 10,000 ppm NaCl solution for 170 hours and again measuring the

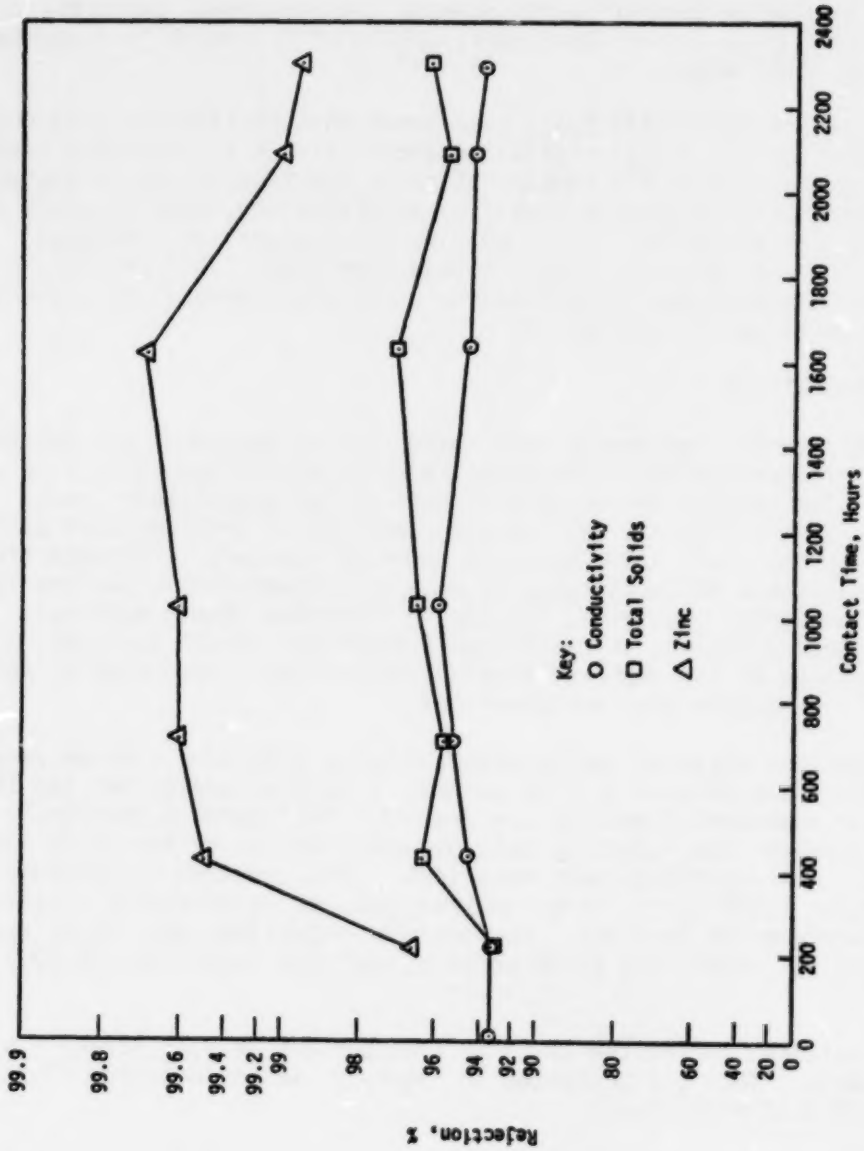


Figure 6. Rejection for membrane J1 at 5% of bath strength.

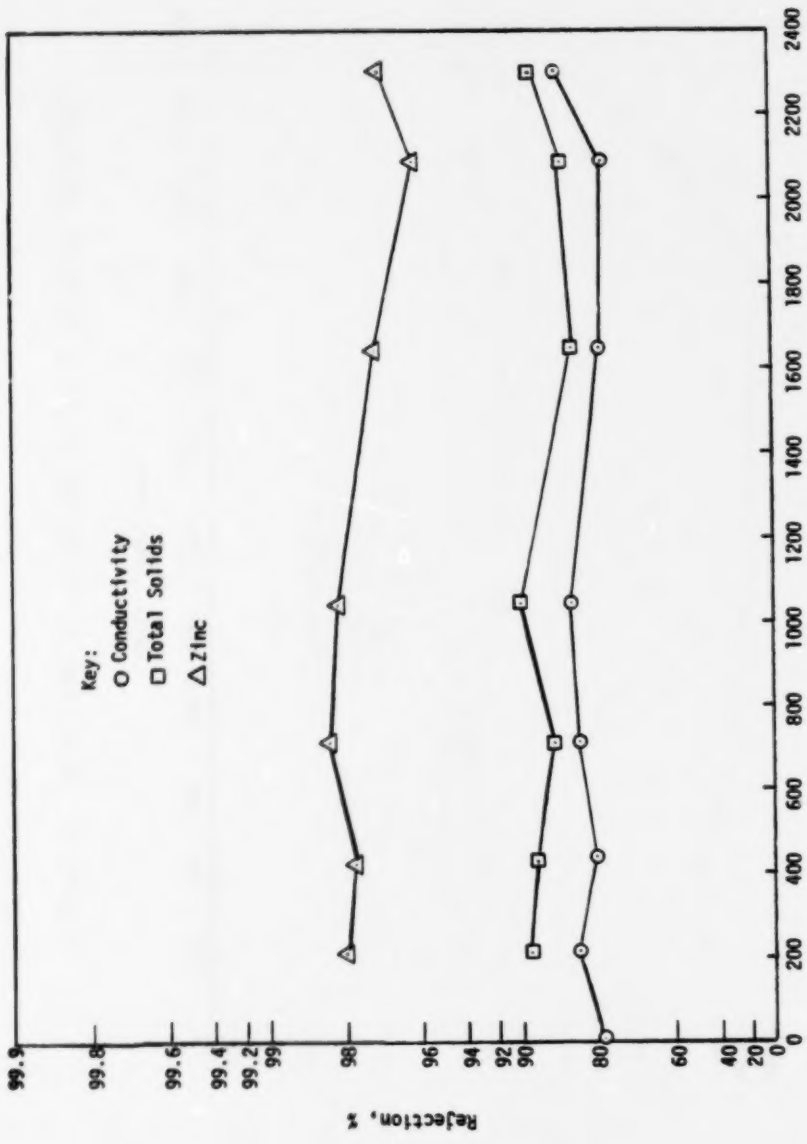


Figure 7. Rejection for membrane J2 at 5% of bath strength.

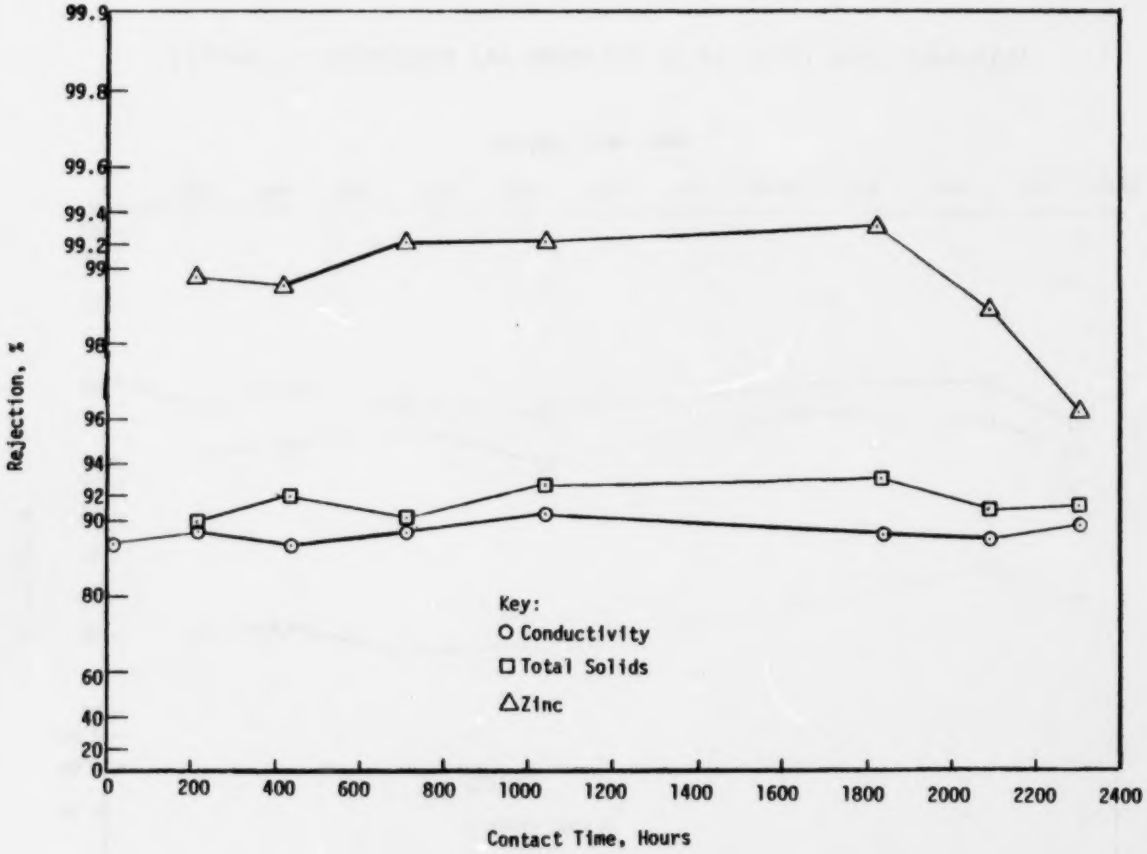


Figure 8. Rejection for membrane J3 at 5% of bath strength.

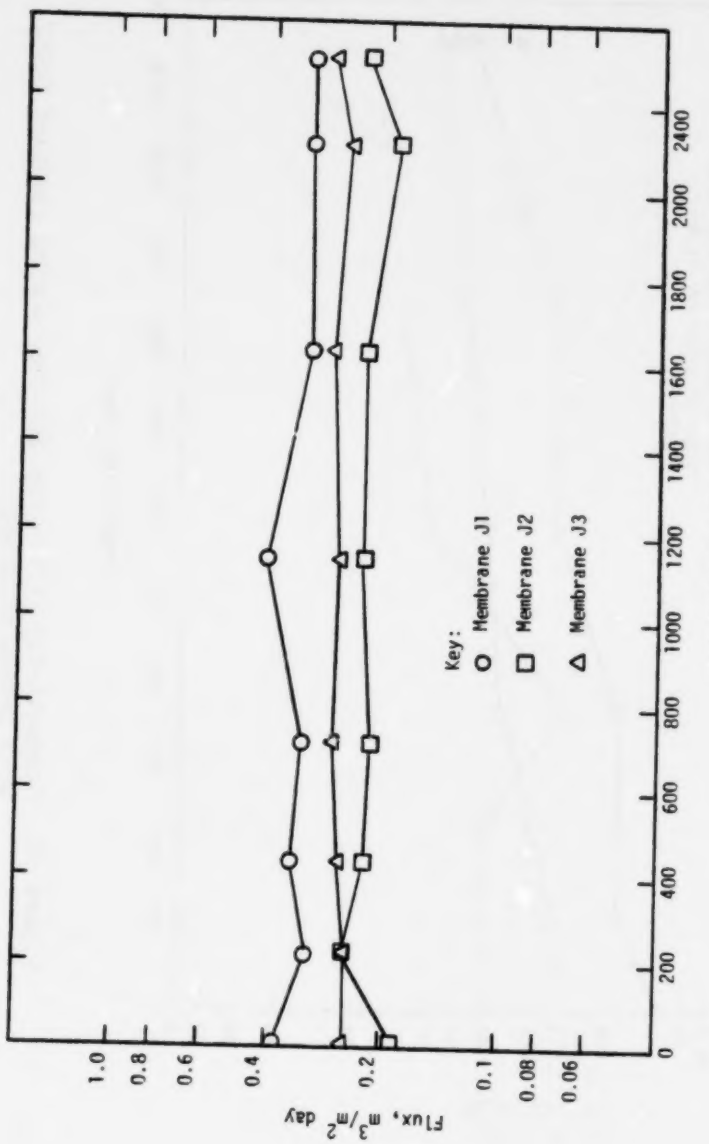


Figure 9. Flux at 5% of bath strength.

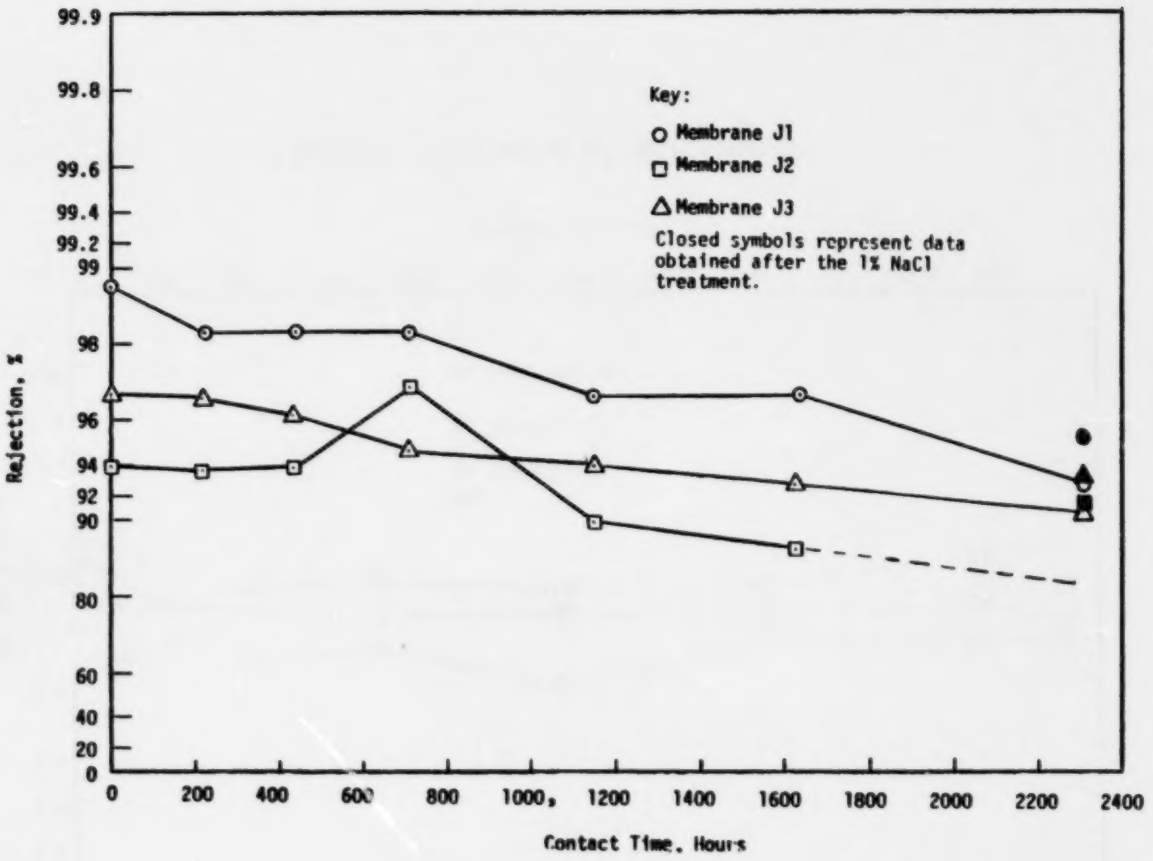


Figure 10. Conductivity rejections obtained during standard tests with sodium chloride.

conductivity rejection with a 1,500 ppm Nacl solution. It was felt that by operating the system at a high salt concentration, the adsorption or ion exchange that had occurred could be reversed. This was indeed the case, as the rejection for all three membranes increased after this treatment (closed symbols, Figure 10). Perhaps further recovery of NaCl rejection might be achieved by operating the system with higher salt concentrations for a longer period of time.

Flux levels remained stable during the tests except for an apparent increase after an elapsed exposure time of 1,600 hours (Figure 11). This may indicate membrane degradation, but it is more likely to be connected with some other phenomenon since no other data indicate degradation of the membrane.

Data obtained while the system was operating on actual zinc cyanide rinsewaters indicate high fluxes and rejections, as shown in Table 1. Membrane fluxes were 0.25-0.41 $m^3/m^2/day$; conductivity rejections were 76-94 percent; total solids rejections were 85-87 percent; and zinc rejections were 95.5-99.3 percent. It should be noted that although the system was operated at 90 percent water recovery, concentrations in the membrane loop were only 2-4 times those in the feed because of the low rejections of the Type I membranes.

Results of the 2,300-hour field test with the tubular NS-100 module indicated adequate flux and rejection and no degradation for the Type J membranes. It is, therefore, concluded that the NS-100 membrane can be used for the treatment of zinc cyanide rinsewaters.

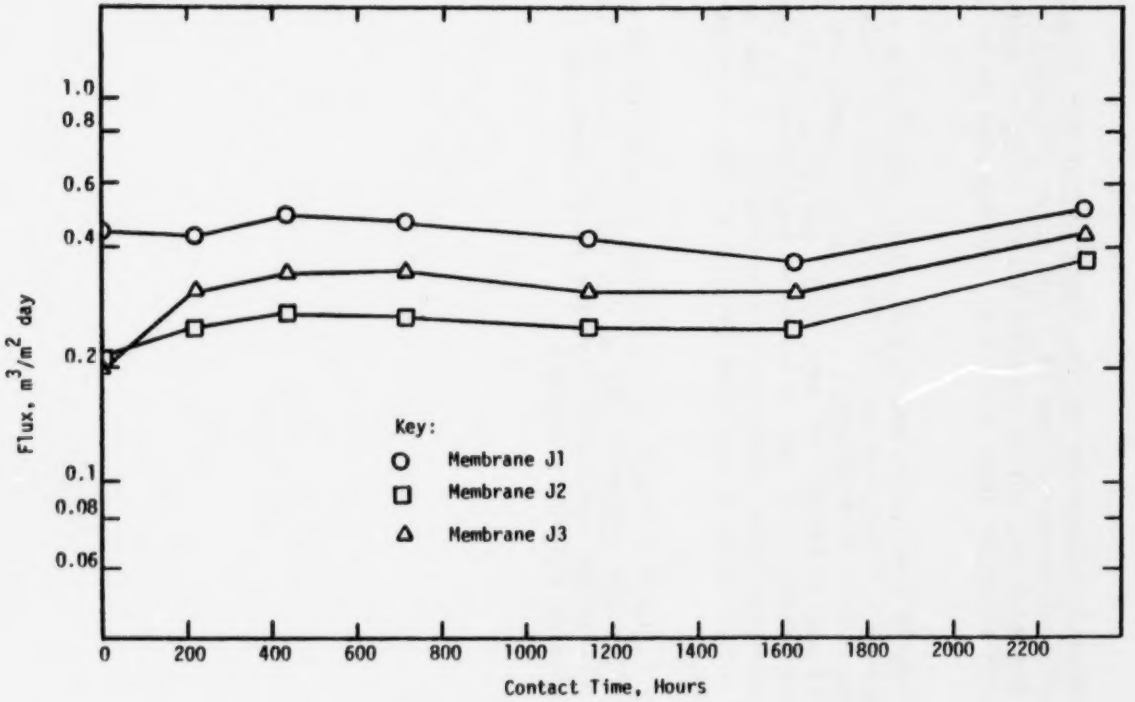


Figure 11. Fluxes obtained during standard sodium chloride tests.

TABLE 1. MEMBRANE PERFORMANCE DURING OPERATION ON ACTUAL ZINC CYANIDE RINSEWATER

Time (hrs)	1,850	2,100
Rinse concentration		
Conductivity (μmho/cm)	9,800	8,000
Total solids (mg/l)	6,843	4,560
Zinc (mg/l)	375	204
Membrane loop concentration		
Conductivity (μmho/cm)	17,000	21,000
Total solids (mg/l)	14,606	18,350
Zinc (mg/l)	980	665
Membrane J1		
Conductivity rejection (%)	94.1	94.3
Total solids rejection (%)	96.2	97.1
Zinc rejection (%)	99.3	99.2
Flux ($m^3/m^2/day$)	0.32	0.39
Membrane J2		
Conductivity rejection (%)	75.9	77.1
Total solids rejection (%)	85.3	86.5
Zinc rejection (%)	96.1	95.5
Flux ($m^3/m^2/day$)	0.24	0.28
Membrane J3		
Conductivity rejection (%)	86.5	88.1
Total solids rejection (%)	92.0	94.1
Zinc rejection (%)	98.7	98.5
Flux ($m^3/m^2/day$)	0.26	0.38

SECTION 6

FABRICATION OF NS-100 SPIRAL-WOUND MODULES

Following the successful field tests with the NS-100 membrane in tubular configuration, further efforts were directed toward fabricating an NS-100 spiral-wound module.

The preparation of NS-100 spiral-wound membrane modules based on formation procedures developed for tubular configurations required adaptations in two main areas:

1. the casting of a continuous flat sheet polysulfone substrate on a cloth backing (rather than the casting of discrete tubular sections)

2. the formation of the NS-100 ultrathin membrane on the flat sheet polysulfone substrate.

A flat sheet of polysulfone, 0.91 m wide by 92 m long, was cast, and two basic approaches to the formation of the NS-100 spiral-wound module were attempted. In the first approach, a polysulfone module was wound and then the NS-100 skin was formed in situ. In the second approach, the NS-100 ultrathin membrane was formed on the polysulfone substrate and then the membrane was wound into a spiral module. One module using the first approach and four modules using the second approach were fabricated. The best performance characteristics obtained during a standard 1,500 mg/l NaCl test were a flux of 0.33 m^3/m^2/day and a rejection of 60 percent. Following these attempts it was concluded that the additional development required to fabricate a workable NS-100 spiral-wound module was beyond the resources available to this program.

Although commercialization of a spiral-wound NS-100 module does not appear imminent, the Fluid Systems Division of Univeral Oil Products, Inc. (San Diego, CA) has recently developed a similar membrane, designated PA-300, in a spiral-wound configuration. This membrane module should be commercially available in the near future and may well supercede the NS-100 as the most promising new membrane for treatment of zinc cyanide and other electroplating rinsewaters. Tests being conducted at the Walden Division of Abcor, Inc., under a separate EPA grant, indicate excellent performance characteristics for PA-300 flat-sheet membranes during exposure to zinc cyanide rinsewaters. Based on these tests and the results presented in Sections 4 and 5 for the NS-100 membrane (given its similarity to the PA-300), field testing of a spiral-wound PA-300 membrane on zinc cyanide rinsewater is recommended. Such a field test is being conducted under a separate EPA grant; results will be published in a separate report.

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